NERL Research Abstract

EPA's National Exposure Research Laboratory
GPRA Goal 2 - Clean and Safe Water

Significant Research Findings

Identification of New Disinfection By-Products Formed by Alternative Disinfectants

Purpose

Trihalomethanes (THMs) and other halogenated by-products can be formed during chlorination of drinking water. Several drinking water treatment plants in the U.S. have altered their treatment methods and adopted alternative disinfectants to comply with an EPA regulation that limits levels of THMs in drinking water. The alternative disinfectants currently being used (including ozone, chloramine, and chlorine dioxide) are effective and do not produce significant levels of THMs. However, limited information exists concerning disinfection by-products (DBPs) that are produced from alternative disinfectants, resulting in significant uncertainty regarding human exposure to DBPs. These alternative disinfectants may produce compounds more or less harmful than those produced by chlorine. The purpose of this research is to identify unknown DBPs formed by alternative disinfectants and in combination with chlorine. This abstract presents a summary of all research NERL has conducted on DBPs from alternative disinfectants.

Research Approach

Drinking water was collected from full-scale treatment plants using ozone and chloramine, and from pilot plants using chlorine dioxide, ozone, and titanium dioxide with UV light—with and without secondary chlorine or chloramine disinfection. Elevated bromide levels was also investigated using drinking water disinfected with ozone. Disinfection by-products were extracted using XAD resins. A combination of analytical techniques, including gas chromatography (GC)/high resolution mass spectrometry (MS), GC/chemical ionization MS, and GC/infrared spectroscopy, were used to identify new DBPs found in drinking water samples. Liquid chromatography (LC)/MS was used to identify polar DBPs that are difficult to extract from water. Derivatization techniques, including pentafluorobenzylhydroxylamine (PFBHA), 2,4-dinitrophenylhydrazine (DNPH), and BF_3/methanol methylations were also utilized to aid in the extraction and identification of DBPs.

Major Findings

Many new DBPs were identified using the combination of spectroscopic techniques. Several DBPs were not present in the spectral library databases, and, therefore, required information obtained from high resolution MS, chemical ionization MS, infrared spectroscopy, and much scientific reasoning. Many identifications were confirmed through the analysis of purchased or synthesized standards. Elevated levels of bromide in the source water had a substantial effect on DBPs formed by ozone-chlorine and ozone-chloramine treatments, shifting the speciation from mostly chlorine-containing species (e.g., trichloronitromethane) to bromine-containing species (tribromonitromethane). Elevated bromide levels had a very minor effect on ozone DBPs formed; only one compound, dibromoacetonitrile, was formed by ozone treatment alone (for pilot plant samples of Mississippi River-treated water). Comparing the DBPs found for the different treatments, TiO_2/UV formed the least amount of by-products, with only a single diketone formed in the treatment studied. Chlorine dioxide and ozone produced the least halogen-containing by-products (only two for chlorine dioxide and one for ozone, under high bromide conditions), whereas chlorine and chloramine formed many halogenated by-products. Most of the by-products were the same for chlorine and chloramine, but chloramine produced lower levels compared to chlorine. This effect has been seen by others when comparing THMs and haloacetic acids formed by the two disinfectants.

Research Collaboration and Publications

Much of this research is the result of a collaboration with a research group at EPA's National Risk Management Research Laboratory (NRMRL). Scientists from NRMRL were responsible for performing some of the treatments studied. Scientists from EPA's NERL were responsible for the identification work. A research brief will be published that summarizes all of the results and compares DBPs for the different disinfectants studied. As this represents results of a large volume of research, there have been several peer-reviewed journal articles published using portions of the work. There have also been presentations resulting in additional publications (two are listed here).

Patterson, K.S., Richardson, S.D., Lykins, B.W., Jr. Mutagenicity of drinking water following disinfection. *Journal of Water Supply: Research and Technology-AQUA* 44: 1-9, 1995.

Richardson, S.D., Thruston, A.D., Jr., Chen, P.H., Collette, T.W., Schenck, K.M., Lykins, B.W., Jr. Identification of Drinking Water Disinfection By-Products from Chlorine Dioxide, Ozone, Chloramine, and Chlorine. EPA Research Brief. In preparation.

Richardson, S.D., Caughran, T.V., Poiger, T., Guo, Y., Crumley, F.G. Application of DNPH derivatization with LC/MS to the identification of polar carbonyl disinfection by-products in drinking water. *Ozone Science & Engineering*: In press.

Richardson, S.D., Thruston, A.D., Jr., Caughran, T.V., Chen, P.H., Collette, T.W., Schenck, K.M., Lykins, B.W., Jr., Rav-Acha, C., Glezer, V. Identification of new drinking water disinfection by-products from ozone, chlorine dioxide, chloramine, and chlorine. In: Environmental Challenges for the Next Millennium: The 7th International Conference of the Israel Society for Ecology and Environmental Quality Sciences. *Water, Air, and Soil Pollution*. In press. (Invited article).

Richardson, S.D., Caughran, T.V., Poiger, T., Guo, Y., Crumley, F.G. Identification of polar drinking water disinfection by-products using LC/MS. Natural Organic Matter and Disinfection By-products, American Chemical Society. In press. (Invited article).

Richardson, S.D., Thruston, A.D., Jr., Collette, T.W., Patterson, K.S., Lykins, B.W., Jr., Majetich, G., Zhang, Y. Multispectral identification of chlorine dioxide disinfection by-products in drinking water. *Environmental Science & Technology* 28: 592-599, 1994.

Richardson, S.D., Thruston, A.D., Jr., Collette, T.W., Patterson, K.S., Lykins, B.W., Jr., Ireland, J.C. Identification of TiO_2/UV disinfection by-products in drinking water. *Environmental Science & Technology* 30: 3327-3334, 1996.

Richardson, S.D., Thruston, A.D., Jr., Caughran, T.V., Chen, P.H., Collette, T.W., Floyd, T.L., Schenck, K.M., Lykins, B.W., Jr. Identification of new ozone disinfection by-products in drinking water. *Environmental Science & Technology* 33: 3368-3377, 1999.

Richardson, S.D., Thruston, A.D., Jr., Caughran, T.V., Chen, P.H., Collette, T.W., Floyd, T.L., Schenck, K.M., Lykins, B.W., Jr. Identification of new drinking water disinfection by-products formed in the presence of bromide. *Environmental Science & Technology* 33: 3378-3383, 1999.

Richardson, S.D., Thruston, Jr., A.D., Caughran, T.V., Chen, P.H., Guo, Y., Collette, T.W., Floyd, T.L., Schenck, K.M., Lykins, B.W., Jr. Identification of new drinking water disinfection by-products formed in the presence of bromide. Natural Organic Matter and Disinfection By-Products, American Chemical Society, 1999. (Invited article).

Future Research

Many new DBPs are being measured in a nationwide study and are also being researched in preliminary health effects studies. The nationwide study will provide an opportunity to analyze a wide range of drinking waters for new DBPs. New research is also being conducted that identifies chlorine dioxide DBPs formed under high bromide conditions (through a collaboration with researchers at the Israel Ministry of Health). This is an important area that has never been studied, yet many people in the U.S., particularly in Texas, drink water treated under these conditions. Research also continues in this area of polar drinking water DBPs. A collaboration with researchers at the University of Torino (Italy) has been initiated to investigate another derivatization procedure that previously has been shown useful for identifying poly-hydroxy, poly-amino, and poly-carboxy polar compounds in water. This method will be developed (to lower detection limits), and real drinking water will be analyzed. Also, there is on-going research focusing on how some polar (and other) DBPs are formed (mechanisms of formation), with the goal of learning how to control the formation of any DBPs determined to be toxic.

Inquiries about new disinfection by-products may be directed to:
Dr. Susan Richardson
U.S. Environmental Protection Agency
960 College Station Road
Athens, GA 30605-2700
Phone: (706)355-8304
E-mail: richardson.susan@epa.gov